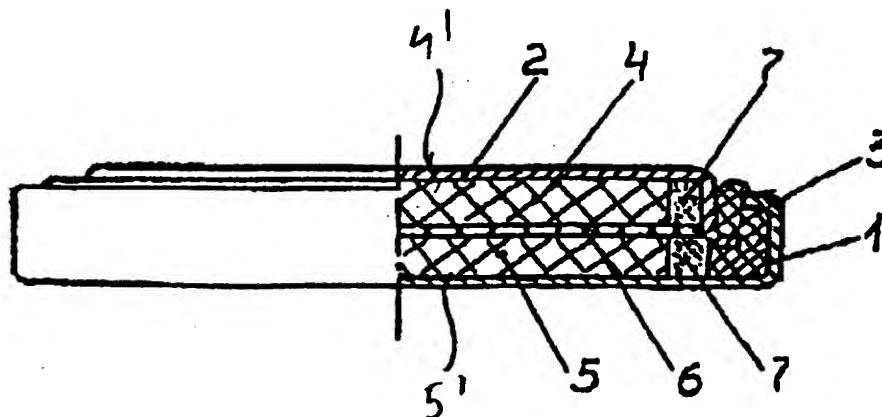




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(54) Title: DOUBLE LAYER CAPACITOR WITH POROUS CARBON ELECTRODES AND METHOD FOR MANUFACTURING THESE ELECTRODES



(57) Abstract

A double electric layer capacitor comprising at least two electrodes (4, 5), substantially of porous carbon, the electrodes being substantially saturated with electrolyte and separated by means of a porous separator (6) with ionic conductivity. The capacitor is especially characterized in that the electrodes (4, 5) in the form of a porous structure are made of materials with a carbon content exceeding 95 % mass and a pore volume exceeding 55 % of the electrode material volume, a certain part of the pores having a size less than 10 nm.

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DOUBLE LAYER CAPACITOR WITH POROUS CARBON ELECTRODES AND METHOD FOR MANUFACTURING THESE ELECTRODES

The present invention relates to an electric device, more specifically to an accumulating construction for electricity, which can be used e.g. as a short time or reserve source of electric current for a radio electronic apparatus, for memory units of personal computers, video and other devices.

The invention also relates to a process of manufacturing a porous carbon material and a capacitor electrode material.

One of the main directions of the development of high-efficiency capacitors with double electric layer is to make new electrode carbon materials with such a combination of properties as an optimal pore size, mechanical strength and high chemical purity.

Previously known are capacitors with a double electric layer (e.g. Japanese patent application No. 3-62296.1991), comprising two polarized electrodes divided by a separator, which are placed in a hermetic frame. The electrodes are made of active carbon and a binding agent, which consists of carbon black and ceramic powder. The electrode material has a porous structure, resulting in a specific electric capacitance not more than 25 F/cm^3 .

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The deficiencies of such capacitors are:

- considerable leakage currents due to a great content of ash in the electrode material (3-8%);
- increased variation in capacitance characteristics due to changes in microporosity properties of the electrode material in the process of manufacture of the electrodes and the capacitor assembly;
- the electrode material has low mechanical strength (this limits the use of these capacitors in constructions, which are working under conditions of high mechanical stress, e.g. vibrations).

Further, previously known are capacitors with double electric layer, comprising a frame of stainless steel; the frame comprises a bottom and a lid joined by a washer creating a hermetic container. In the frame, two polarized electrodes, saturated with electrolyte and separated by a porous separator, are situated. The electrodes are made of active carbon (80% mass) and a binding agent, which consists of ash (10% mass) and polytetrafluorethylene (10% mass). The material in the form of paste is applied to an electrically conductive underlayer and is then rolled and dried. From the resulting sheet product the prescribed size electrodes are cut.

Such capacitors can operate over a wide range of temperatures. The electrode material provides specific electric

capacitance within the limits of 20-25 F/cm³. However, these capacitors have all the deficiencies of the preceeding ones.

The object of the present invention is to obtain a simultaneous increase in capacitor specific electric capacitance, decreased variation of the actual capacitance values and decrease in leakage currents. In addition, the purpose of the invention is to obtain an increase in electrode strength and mechanical stability. This will allow an extension of the field of use for the capacitors, for example in constructions working under conditions of mechanical impact or vibration. To obtain this technical result the capacitor with double electric layer, within a hermetic frame, in which at least two polarized electrodes of porous carbon are situated, saturated with electrolyte and separated by means of a separator with ionic conductivity, have the electrodes in the form of a structure made of material with carbon content more than 95% mass, preferably more than 99% mass. The material has a total pore volume preferably in the range from 55 to 80% of the electrode volume, the volume of pores with nanopore sizes less than 10 nm preferably being 35-50% of the electrode volume; this makes it possible to obtain a high electric capacitance.

According to a preferred embodiment these electrode properties are obtained by means of a special chemothermal

treatment of a metal carbide composite. After such a treatment the electrode contains practically pure carbon with a ramified system of transport channels/pores, and only minor amounts of impurities (less than 5% mass, preferably less than 1% mass). These electrodes have a carbon structure providing high electrode mechanical strength (compressive strength more than 90 kg/cm²). The material consists of a solid network of carbon interconnected throughout the structure, resulting in mechanical rigidity and strength, and a combination of coarser sized transport channels/pores of the electrolyte and nano sized porosity, together making up the total porosity volume. Of importance is also the stability of the electrode dimensions and its pores and, as a result, a stability of the electrode electrical properties. Thus, the decrease in height and diameter values from intermediate product to finished electrode is not more than 0,05% permitting a very limited variation in electrode specific electric capacitance, resulting in actual capacitor capacitance in the range $\pm 15\%$, whereas known capacitors have the electric capacitance tolerance $+ 80$ to $- 20\%$.

The new electrodes offer an increase in specific electric capacitance and actual capacitor capacitance by nearly 30% in comparison with known technical solutions and a decrease in leakage currents of 5-10 times because of an only minor impurity content of the electrode material. In addition, the high electrode strength makes it possible to use the

capacitors in devices working under vibration, impact and other mechanical stresses.

The invention will now be described in more detail with reference to exemplifying embodiments thereof and also with reference to the accompanying drawing, in which in figure 1 an overall capacitor picture is given (side view) and in figure 2 plots of the voltage across the load versus discharge time are given.

The capacitor with a double electric layer comprises a hermetic frame, comprising a bottom 1 and a lid 2, joined by a dielectric washer 3. Inside of the frame electrodes 4, 5 are situated. The electrodes are saturated with an electrolyte and separated by means of a porous separator 6. The opposite sides 4', 5' of the double electrode layer are in contact with the bottom 1 and lid 2 respectively. To make assembly of the capacitor more simple there are elastic washers 7 encircling the electrodes peripherally.

For confirmation of the obtained technical result 12 pieces of carbon electrodes (diameter 19.5 mm, height 1.0 mm) and 6 pieces of button like capacitors (diameter 24.5 mm, height 2.2 mm) were manufactured. As a separator porous polypropylene with ionic conductivity was used and as electrolyte an aqueous solution of alkali, KOH, was used. The nominal electric capacitance of the capacitor was 20F and the voltage was 1.0 volt.

The physical and mechanical properties of the electrode material were investigated and the capacitors were tested for reliability and possibility to work under actual conditions as a power source for electronic watches and electronic memory units for personal computers. The tests for the reliability were carried out at the voltage 0.9 ± 0.1 V. at a temperature of $+70 \pm 5^\circ$ C. The test duration was 500 hours.

The results of the investigation of the electrode physical, chemical and mechanical properties and of the capacitor tests are given in tables 1 and 2 and by the graphs of figure 2.

An analysis of the results of electrode investigation (table 1) shows that the volume of the pores with a size less than 10 nm (average 43% of electrode volume) is nearly twice that parameter of carbon electrodes manufactured by means of traditional technology. The compressive strength increased more than 3 times. The specific electric capacitance (average $34,5 \text{ F/cm}^3$) exceeds by nearly 30% the specific capacitance of known carbon materials (not more than 25 F/cm^3).

The results of the test of reliability (table 2) show only slight variation of the nominal capacitor capacitance ($\pm 5,3\%$). The explanation for this is the high mechanical strength of the carbon electrodes, having a stable ramified structure, maintaining geometrical and electrode and elec-

trolyte parameters during the assembly process.

After the test the capacity loss was 5,7% (average) and the increase in inner resistance was 18% (average), satisfying high performance demands.

The results of the test of capacitors show (Fig. 2) that the duration of the performance of the capacitors as a current source was: 198 hours at the load 100 kohm, 32 hours at the load 50 kohm, 3 hours at the load 20 kohm and 2 hours at the load 0,5 kohm. These data imitate the real discharge of capacitors in operation under load in various devices, where the capacitors may be used as a power source.

According to a preferred embodiment the electrodes are produced from silicon carbide powder and, as a binding agent, a mixture consisting of carbon black, phenolformaldehydic resin and ethylated alcohol in the following components correlation, mass.%:

Carbon black	30-50
Phenolformaldehydic resin	5-10
Ethylated alcohol	40-60

or pyrocarbon in the amount of 5-50 g per 100 g of silicon carbide. After moulding, the blank is saturated by liquid silicon at the temperature of 1450-1700° C. Thermochemical treatment by chlorine is conducted at a temperature of 900-1100° C.

The method is described below:

From silicon carbide powder and the binding agent a blank of given form is moulded. During moulding silicon carbide powder is mixed with a suspension, the composition, mass. %, of which is: carbon black 30-50, phenolformaldehydic resin 5-10, ethylated alcohol 40-60, in the amount of 5-50 g per 100 g of silicon carbide. From this charge the blank is moulded. Then for curing the resin, heat treatment at a temperature of 150° C is conducted. As an alternative a pyrocarbon binding agent, added to silicon carbide powder or introduced by heat treatment in a natural gas current, is used.

Moulded by this method or another moulding technique the blank is placed in a vacuum furnace, where saturation by liquid silicon at a temperature of 1450-1700° in vacuum is made. During this process a chemical interaction of liquid silicon and carbon (carbon black or pyrocarbon) with the formation of secondary silicon carbide takes place. This secondary silicon carbide forms throughout all volume of the blank a continuous structure, bonding the grains of initial silicon carbide and forming a solid silicon carbon body with residual pores filled with silicon metal. The reaction of silicon carbide formation at a temperature lower than 1450° C does not occur and the purpose of the method is not achieved. Silicon begins to evaporate in the vacuum furnace at temperatures above 1700° C. Thus, a porousless blank, comprising silicon carbide particles

bonded by a structure of secondary silicon carbide and free silicon, is obtained. Then the blank is heat treated by chlorine at a temperature of 900-1100° C. During chloration the free silicon metal is removed from the blank in the form of gaseous silicon chloride and thus a necessary volume of transport microporosity channels/pores are formed. Additionally, as a result of silicon carbide chloration, carbon with a developed nanoporous structure is formed.

The combination of transport channels/pores and nanoporosity of the resulting solid carbon network is of great importance, because it facilitates electrolyte access to large available internal electrode surfaces, made up by the nano pore walls. The solid continuous carbon network also provides low internal electrical resistance.

The function of the capacitor according to the invention should be apparent from the specification given above.

The capacitor according to the invention offers considerable advantages compared to previously known techniques as described in the introductory part of the specification.

The invention has been described with reference to an exemplifying embodiment. It will be understood, however, that other embodiments and minor modifications are conceivable without departing from the inventive concept.

For example more than two electrodes may be provided in the capacitor.

Further, it is possible to produce the electrode material by means of some other method that provides a structural network of solid carbon with transport channels/pores and nano porosity resulting in the mentioned advantages. The techniques are preparation of a mould comprising metal carbide, organic binders and carbon, e.g. in the form of carbon black or as a pyrolysis product, and metal infiltration and high-temperature reactions, followed by thermochemical removal of the metal to form the wished solid carbon structure comprising transport channels/pores and nano porosity.

An example might be the use of aluminum carbide and aluminum metal which lowers the needed reaction temperatures in the first process step significantly. So called cubic metal carbides based on Ti and other metals of group IV, V or VI of the periodic system might also be used where gaseous metal halogenes are formed, like fluorides and chlorides.

Test results of electrode material

Table 1

Elec- trodes	Total pores volume in electrodes volume	Volume of pores with sizes less than 10 nm	Specific capaci- tance	Compressive strength	Carbon content
No	%	%	F/cm ³	kg/cm ²	% mass
1	55	45	35	95	99,1
2	70	40	30	99	99,2
3	65	50	39	94	99,3
4	60	45	36	92	99,5
5	75	45	38	93	99,4
6	80	35	31	97	99,2
7	55	50	33	96	99,6
8	75	50	39	100	99,1
9	65	35	30	102	99,3
10	80	45	38	98	99,5
11	60	40	34	97	99,2
12	58	46	35	99	99,4

Test results of manufactured capacitors

Table 2

Capaci- tors	Before test		After test			
	Actual capaci- tance	Resi- stance	Actual capaci- tance	Resi- stance	$\frac{Co-Cl}{Co} \times 100$	$\frac{Rl-Ro}{Rl} \times 100$
No	Co, F	Ro, Ohm	Cl, F	Rl, Ohm	%	%
1	19	0,3	17,8	0,35	6,3	16,6
2	20	0,25	18,6	0,3	7,0	20,0
3	19,5	0,35	18,0	0,4	7,6	14,3
4	18,5	0,25	18,0	0,3	2,8	20,0
5	18,0	0,3	17,0	0,35	5,6	16,6
6	19,5	0,25	18,5	0,3	5,1	20,0

Claims

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1. A double electric layer capacitor comprising at least two electrodes, substantially of porous carbon, the electrodes being substantially saturated with electrolyte and separated by means of a porous separator with ionic conductivity, characterized in, that the electrodes (4, 5) in the form of a porous structure are made of materials with a carbon content exceeding 95% mass and a pore volume exceeding 55% of the electrode material volume, a certain part of the pores having a size less than 10 nm.
2. A capacitor according to claim 1, characterized in, that the carbon content exceeds 99% mass.
3. A capacitor according to claim 1 or 2, characterized in that, the volume of pores falls in the range 55 - 80%, preferably in the range 60 - 80%.
4. A capacitor according to claim 1, 2 or 3, characterized in, that the volume of pores having a size less than 10 nm is 35-50% of the electrode material volume.
5. A capacitor according to claim 1, 2, 3 or 4, characterized in, that the compressive strength of the electrode material exceeds 90 kg/cm².
6. A capacitor according to claim 1, 2, 3, 4 or 5, characterized in that, the electrodes are made from metal carbide powder and, as a binding agent, organic binders and

carbon, e.g. in the form of carbon black or as a pyrolysis product, the amount of binding agent preferably being 5 -50 g per 100 g of metal carbide powder, an electrode blank being moulded from the metal carbide powder and the binding agent.

7. A capacitor according to claim 6, **characterized in**, that said electrodes are made from blanks by means of a chemothermal treatment comprising the steps of

- saturation by liquid metal at a temperature exceeding the melting temperature but not exceeding 300 ° C above this temperature in a vacuum furnace.

- heat treatment in halogen gas, such as fluorine or chlorine, at a temperature of 800 - 1200° C for the formation of the transport channels/pores and nano porous (<10 nm) carbon structure.

8. A capacitor according to claim 6 or 7, **characterized in**, that the metal is from group IV, V or VI of the periodic system or aluminum or silicon.

9. A capacitor according to claim 1, 2, 3, 4, 5, 7 or 8, **characterized in**, that each electrode is made from a blank substantially comprising silicon carbide and a binding agent by means of a chemothermal treatment.

10. A capacitor according to claim 9, characterized in, that the electrodes are made from silicon carbide powder and, as a binding agent, either a mixture substantially comprising 30-50% mass of carbon black, 5-10% mass of phenolformaldehydic resin and 40-60% mass of ethylated alcohol, or pyrocarbon, the amount of binding agent preferably being 5-50 g per 100 g of silicon carbide powder, an electrode blank being moulded from the silicon carbide powder and the binding agent.

11. A capacitor according to claim 9 or 10, characterized in, that said electrodes are made from blanks by means of a chemothermal treatment comprising the steps of

- saturation by liquid silicon at a temperature of 1450-1700° C in a vacuum furnace,

- heat treatment by chlorine at a temperature of 900-1100° C for the formation of the transport channels/pores and nano porous (<10 nm) carbon structure.

12. A capacitor according to any one of the preceeding claims, characterized in, that the electrodes are arranged in a hermetic frame comprising a bottom (1) and a lid (2) joined by means of a dielectric washer (3).

13. A capacitor according to any one of the preceeding claims, characterized in, that elastic washers (7) are provided, encircling the electrodes peripherally.

14. A capacitor electrode material, characterized by interconnecting solid carbon network comprising a combination of transport channels/pore and nano porosity (< 10 nm).

15. A material according to claim 14, characterized in, that the carbon content exceeds 95% mass, preferably 99% mass.

16. A process of manufacturing a porous carbon material as a capacitor according to any one of the preceeding claims, characterized by generation of an electrode structural network of solid carbon by making an electrode from a blank substantially comprising metal carbide powder and a binding agent by means of chemothermal treatment.

Fig. 1

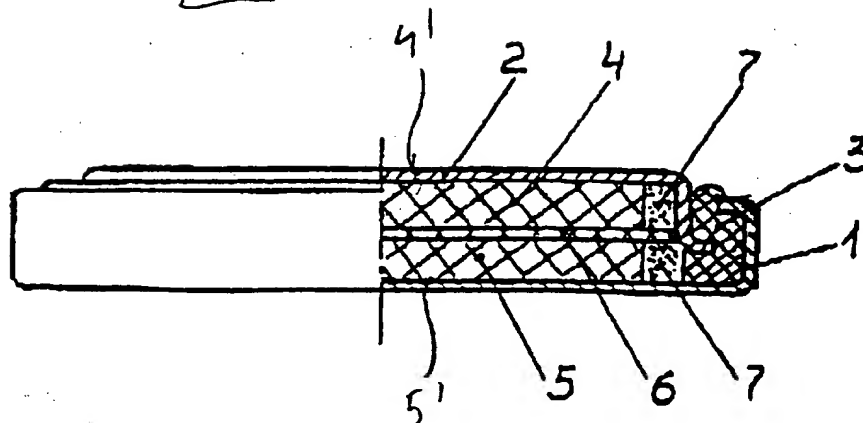
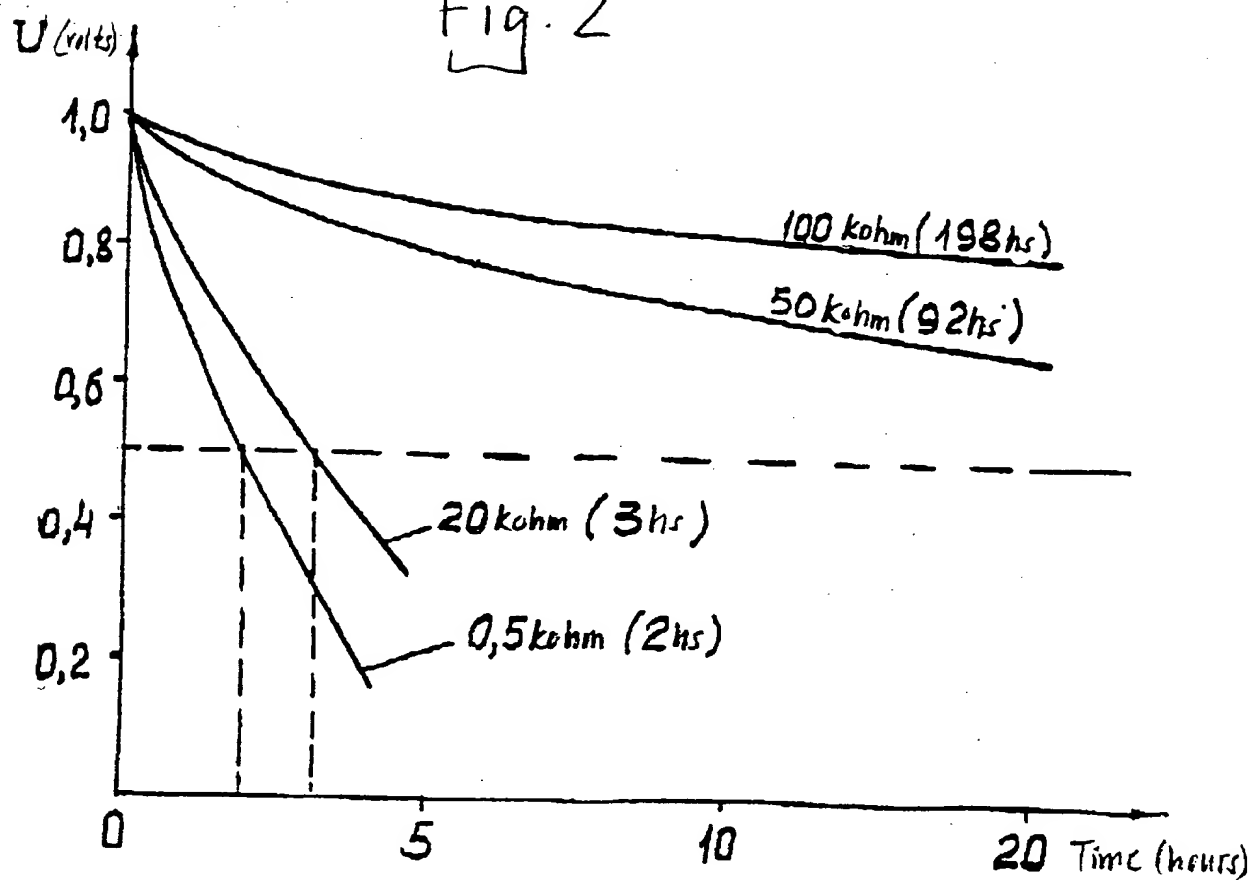


Fig. 2



INTERNATIONAL SEARCH REPORT

Inter. Application No.
PCT/EP 96/00431

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01G9/155

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 660 345 (NISSHINBO INDUSTRIES, INC.) 28 June 1995 see page 2, line 51 - page 3, line 2 see page 3, line 17 - line 22 see page 3, line 48 - page 4, line 29	1,3,4,15
X	---	14
A	PATENT ABSTRACTS OF JAPAN vol. 15, no. 78 (E-1037), 22 February 1991 & JP,A,02 297915 (MITSUI PETROCHEM IND LTD), 10 December 1990, see abstract -----	1,12,13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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